Final Summary Report

Contract Period: June 30, 1960 - June 30, 1961

UNCLASSIFIED

Study of the Molecular Stress Response of Solid Polymers by Photoelastic Methods

(Unclassified Title)

by

R. D. Andrews, Jr.
Chief Investigator

February 15, 1963

Contract Number: DA-19-020-ORD-5213

Project Number: TB4-002

Item Nomenclature: Effect of Combined Stresses on Mechanical Properties of Plastics

Massachusetts Institute of Technology
Memorial Drive, Cambridge, Massachusetts

For

Feltman Research and Engineering Laboratories
Picatinny Arsenal, Dover, New Jersey

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ABSTRACT

The molecular stress response of solid amorphous polymers was studied by measurements of the stress-optical coefficient (SOC) of several types of polymers as a function of temperature. Effects of stereospecific structure were investigated with polymeth l methacrylate (isotactic, syndiotactic, stereo-block, atactic) and polystyrene (isotactic, atactic). The alpha-methyl effect was investigated using polymethyl acrylate, methyl acrylate/ methyl methacrylate copolymer (50/50), polymethyl alpha-chlor acrylate and poly alpha-methyl styrene as comparison materials. Plasticizer effects were studied with polymethyl methacrylate containing 5, 10, and 15% dibutyl phthalate, and elastic modulus measurements were carried out to complement the stress-optical data. Copolymers of ethyl acrylate/methyl methacrylate (9/93 and 13/87) and acrylonitrile/styrene (25/75) were also investigated.

The effect of molecular weight and absorbed moisture on SOC and elastic modulus at room temperature was investigated for polymethyl methacrylate. Room temperature SOC measurements were made on stereospecific poly (t - butyl acrylate), biaxially oriented polymethyl methacrylate sheet and epoxy resin.

An electronic Senarmont birefringence compensator was developed which gives approximately 60 times the precision of the visual Senarmont compensator. Improvements in the technique of low-temperature SOC measurements allow the temperature to be varied continuously from room temperature to liquid nitrogen.

FOURTH QUARTER

Stress-Optical Measurements

1. A styrene/acrylonitrile copolymer (containing 25.3% acrylonitrile by weight) was obtained in the form of a compression - molded sheet from the Plastics division of Monsanto Chemical Co. in Springfield, Mass. This was an experimental polymer which has an improved impact strength over ordinary polystyrene.

A curve of stress-optical coefficient (SOC) vs. temperature over the range - 196°C to +90°C was obtained for this polymer. The resulting curve is similar to that for polystyrene, as would be expected, but also shows some differences. The material has a lower positive SOC in the glassy state than ordinary polystyrene and also has a more constant value vs. temperature (the SOC is about + 9 Br. at - 196°C). Also, the curve shows an inflection in the range of + 50 - 80°C., in such a way that the curve is displaced upward to higher positive values above this temperature range. It seems likely that this effect is due to the acrylonitrile component, since it occurs approximately at the glass transition temperature of polyacrylonitrile.

The effect would probably be more pronounced in a copolymer containing a higher percentage of acrylonitrile, and an attempt will be made in future work to obtain such a copolymer. A series of copolymers covering the entire composition range would be of even greater value.

2. Some samples of biaxially oriented polymethyl methacrylate (PMMA) sheet, produced by different quenching procedures were obtained from the Rohm and Haas Co. These were prepared from Plexiglas II UVA sheet and were strained approximately 100% in the two directions. Comparative measurements of SOC on these materials were made at room temperature (+27°C), with the following results:

	SOC (Br.)
Normally cooled	-3.5
Rapidly cooled with air	-3.4
Cooled with water spray	-1.0

The SOC values for the first two samples are essentially identical with that of unoriented Plexiglas II UVA sheet; the orientation thus seems to have very little effect on the SOC value. However, the value for the water-cooled sample is significantly different from the normal value. It would therefore appear that rapid quenching has more effect on the SOC than molecular orientation. This is somewhat surprising, since previous work on polystyrene has shown that molecular orientation produces a significant change in the value of the SOC. Perhaps the effect of the quenching here is due to a greater amount of free volume frozen into the glassy material, which allows the ester side groups to rotate more easily when the material is strained, producing an algebraically more positive (smaller negative) SOC.

3. The SOC of a sample of epoxy resin (made from a 50/50 mixture of Shell Epon 828 and X71) was measured at room temperature. The extremely high value of + 81 Br. was obtained. This is considerably higher than the glassy state SOC values obtained from any of the other polymers studied in this project. It is suspected that the high value observed for this material is due to the presence of aromatic (phenylene) rings in the chain backbone, rather than as a side group. These come from the Bisphenol A component.

A related material (with phenylene rings in the chain backbone) is Mylar film (du Pont). The aromatic rings come from the terephthalic acid which is reacted with ethylene glycol to form the polymer. This material gives the highest values of orientation birefringence which we have yet observed -- birefringence values lying in the second decimal place (0.01 or 0.02, e.g.). This type of molecular structure is apparently capable of producing very large birefringence effects.

4. Toward the end of the quarter we received some samples of special aromatic - acrylic polymers from the B.F. Goodrich Co. These were polymers which they had prepared for use in a study of the high-energy radiation resistance of polymers as a function of molecular structure. The five polymers received were the following:

poly (4 - phenyl butyl methacrylate)
poly (phenyl 2 - phenyl acrylate)
poly (ethyl 2 - phenyl acrylate)
poly (phenyl 2 - (4 phenyl butyl) acrylate)
poly (β - naphthyl acrylate)

Unfortunately these materials were not in a form suitable for our birefringence measurements; they were in the form of powder or granules, and the quantity was small in every case. It will be necessary to make moldings or solvent - cast films in order to make measurements on these materials, and we did not have time to do this before the termination of the contract.

Modulus Measurements

Modulus measurements as a function of temperature were carried out on the plasticized PMMA samples (containing 5, 10 and 15% dibutyl phthalate), on which SOC measurements were carried out previously. The temperature range covered was from liquid nitrogen temperature (- 196°C.) to room temperature or somewhat above.

Some difficulties were encountered in these measurements. First, significant time effects were observed in many cases. This meant that deflections after a certain arbitrary time of loading (30 sec.) had to be taken as defining the modulus value. Delayed recovery was also observed, which meant that it was necessary to wait for a few minutes after one loading before applying the next load. As a result these measurements were very slow and time-consuming.

Second, there seemed to be some difficulties with absorption of the acetone and pentane used as cooling liquids. When the plasticized samples were removed from these liquids after an experiment, and weighed as a function of time, a gradual loss of weight was generally observed, indicating the evaporation of absorbed solvent. It seems probable that there was some extraction of plasticizer as well, particularly at the surface.

Despite these problems, it was clear that plasticizer had a significant effect on the modulus. Unplasticized PMMA shows an unusually large change of modulus with

temperature in the glassy state (from liquid nitrogen temperature to room temperature, for example). A relatively flat region of the modulus vs. temperature curve is seen at the lowest temperatures; above that, the modulus decreases as almost a straight line over a considerable temperature range. Increasing plasticizer lowers the low-temperature plateau value and lowers the temperature range where the linear drop in modulus takes place; this latter is probably related to the effect of the plasticizer in lowering the glass transition temperature.

Equipment

1. A new technique of temperature control was evolved for the cold chamber used to make low-temperature SOC measurements. It was found that simply by adding different amounts of liquid nitrogen to the double-walled metal jacket, the temperature would stabilize to various values, and the temperature would remain constant within 1-2 ^{o}C for 30-40 minutes -- long enough to make an SOC determination. This is a consequence of the very good insulation of the chamber. The temperature could be taken down in steps in this way, all the way to liquid nitrogen temperature.

This represents an important advance in technique since in this way all temperature values between room temperature and liquid nitrogen temperature are available; we are no longer restricted to a few fixed points. Also, the inconvenience and problems of possible effect on the sample encountered when fixed-point fluids are used, are entirely eliminated. The use of the external temperature supply mentioned previously (Tenney unit) is also no longer needed.

2. The electronic Senarmont compensator equipment was completed in this quarter, and its performance checked out. The optical bench was completed and the electronic circuitry (power supply for photomultiplier, oscillater, tuned amplifier, and gate-and-integrating circuit) were incorporated into a relay rack, for convenience and mobility. Read-out was tried with both an oscilloscope and a vacuum-tube voltmeter. The latter seemed to give the greater accuracy, as well as being more convenient; with the voltmeter it is possible to see which side of the null point you are on.

Precision of determination of the null point by the rotating analyzer was within about 6 seconds of rotation angle, where the rotation involved was small enough so that the precision micrometer rotator could be used. A precision of about 0.1 degree in the analyzer rotation angle can be obtained with the usual visual Senarmont compensator, by taking an average of a few readings (3 to 5 duplicate readings have normally been used); this would correspond to 6 minutes of rotation. The electronic equipment therefore provides an accuracy approximately 60 times that of the visual method, which is a substantial improvement. The equipment in general has been found to function very well. It may also be noted that the equipment can be used not merely as a device for measuring birefringence, but also in a more general way as a high-precision polarimeter and ellipsometer.

A general view of the various parts is shown in Fig. 1. The arrangement of the optical bench for use as a Senarmont compensator is shown in Fig. 2. And typical raw data in a plot representing effectively birefringence vs. stress for a sample of PMMA is shown in Fig. 3; the lack of scatter in the points is very evident here.

Note: A detailed description of the construction and operation of this equipment, including theory and a discussion of errors, is available as an M.I.T. Plastics Research Laboratory report, "A New High Precision Photoelectric Universal Polarimeter" by Weingart, Williamson and Andrews (May 31, 1961), and can be obtained from the writer of the present report (R.D.A.)

SUMMARY OF WORK CARRIED OUT UNDER PRESENT CONTRACT (12-month period)

Stress-Optical Measurements

A. Over Temperature Range
   1. Stereospecific polymethyl methacrylate (isotactic, syndiotactic, stereo-block)
   2. Stereospecific polystyrene (isotactic)
   3. Polymethyl acrylate vs. polymethyl methacrylate
   4. Methyl acrylate/methyl methacrylate copolymer (50/50)
   5. Ethyl acrylate/methyl methacrylate copolymers (9/93 and 13/87).

6. Poly (methyl alpha-chlor acrylate)
7. Plasticized polymethyl methacrylate (5, 10, 15% dibutyl phthalate)
8. Poly (alpha-methyl styrene)
9. Styrene/acrylonitrile copolymer (75/25)

B. At Room Temperature
1. Stereospecific Poly (t-butyl acrylate)
2. Polymethyl methacrylate -- different Mol. Wts.
3. Polymethyl methacrylate -- humidity effect.
4. Biaxially oriented polymethyl methacrylate sheet.
5. Epoxy resin (Epon 828/X71)

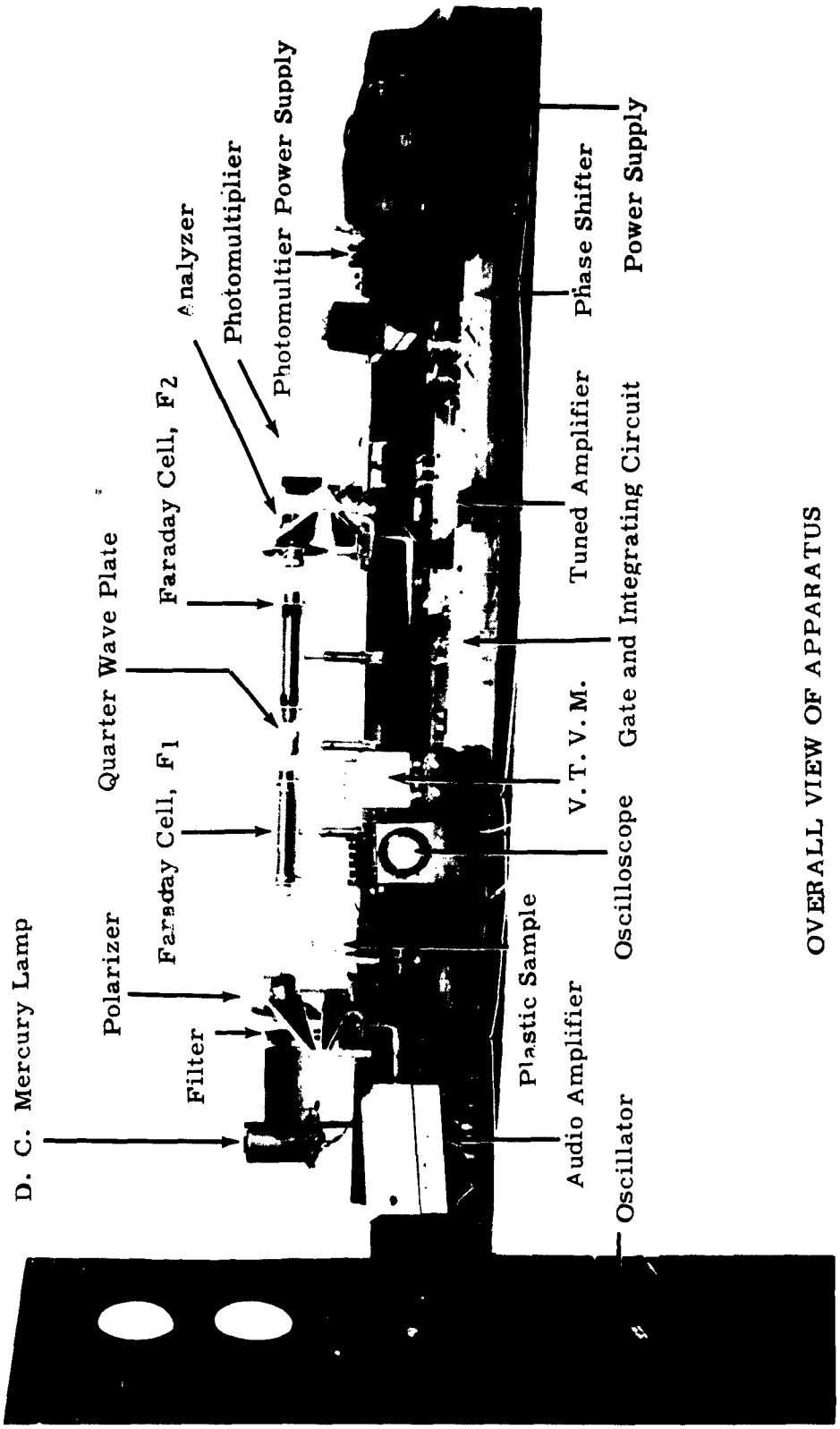
Modulus Measurements

A. Over Temperature Range
1. Plasticized polymethyl methacrylate (5, 10, 15% dibutyl phthalate)

B. At Room Temperature
1. Polymethyl methacrylate -- Mol. Wt. series
2. Polymethyl methacrylate -- humidity treatment

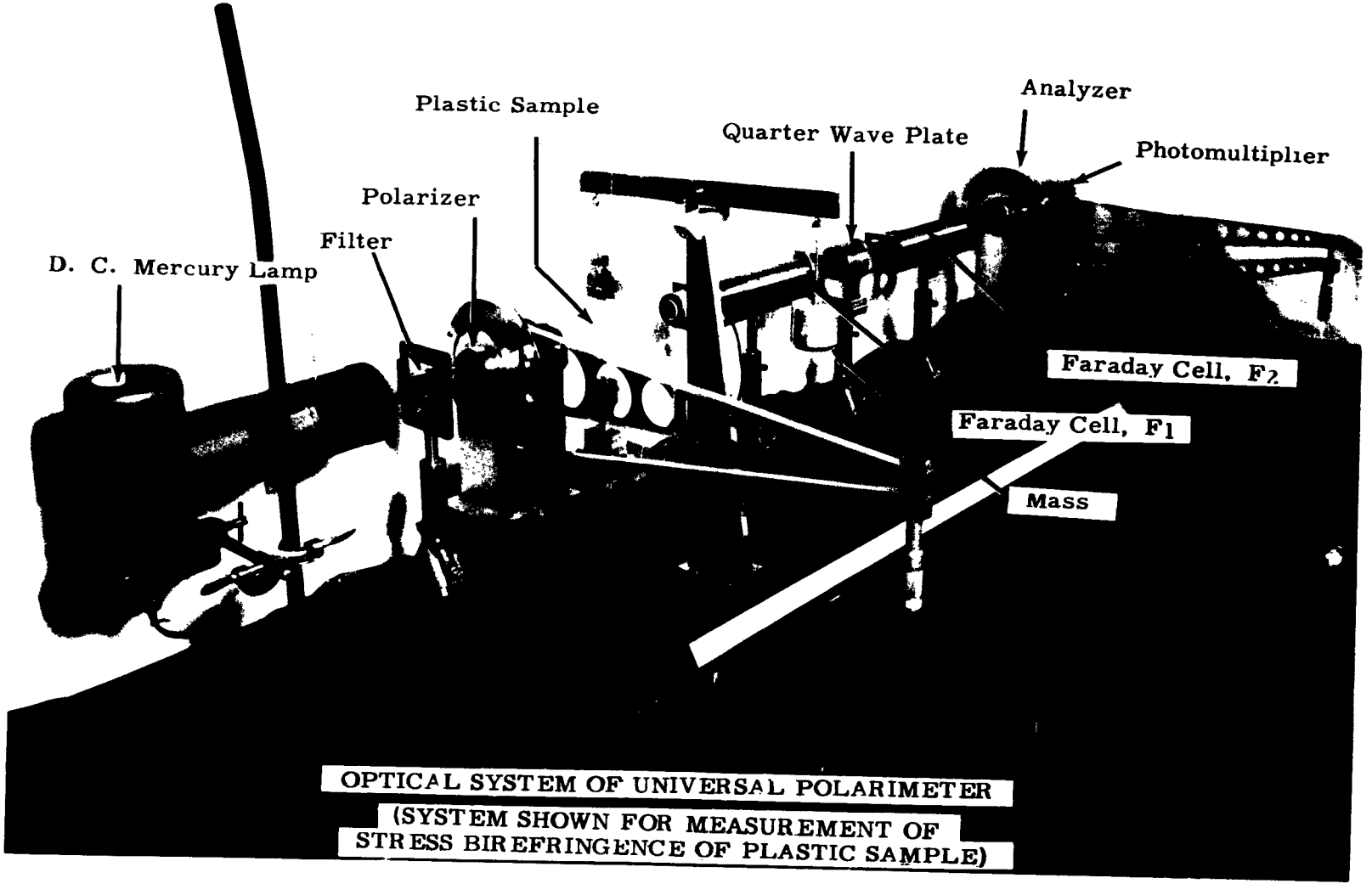
Equipment and Experimental

1. Development and construction of high-precision electronic Senarmont compensator equipment.
2. Modification of low-temperature unit to allow use of Tenney temperature control unit down to -50°C.
3. New technique for use of liquid nitrogen to give complete range of low temperatures in the low-temperature unit from room temperature down to liquid nitrogen temperature.



OVERALL VIEW OF APPARATUS

FIG. 1



OPTICAL SYSTEM OF UNIVERSAL POLARIMETER
(SYSTEM SHOWN FOR MEASUREMENT OF STRESS BIREFRINGENCE OF PLASTIC SAMPLE)

FIG. 2

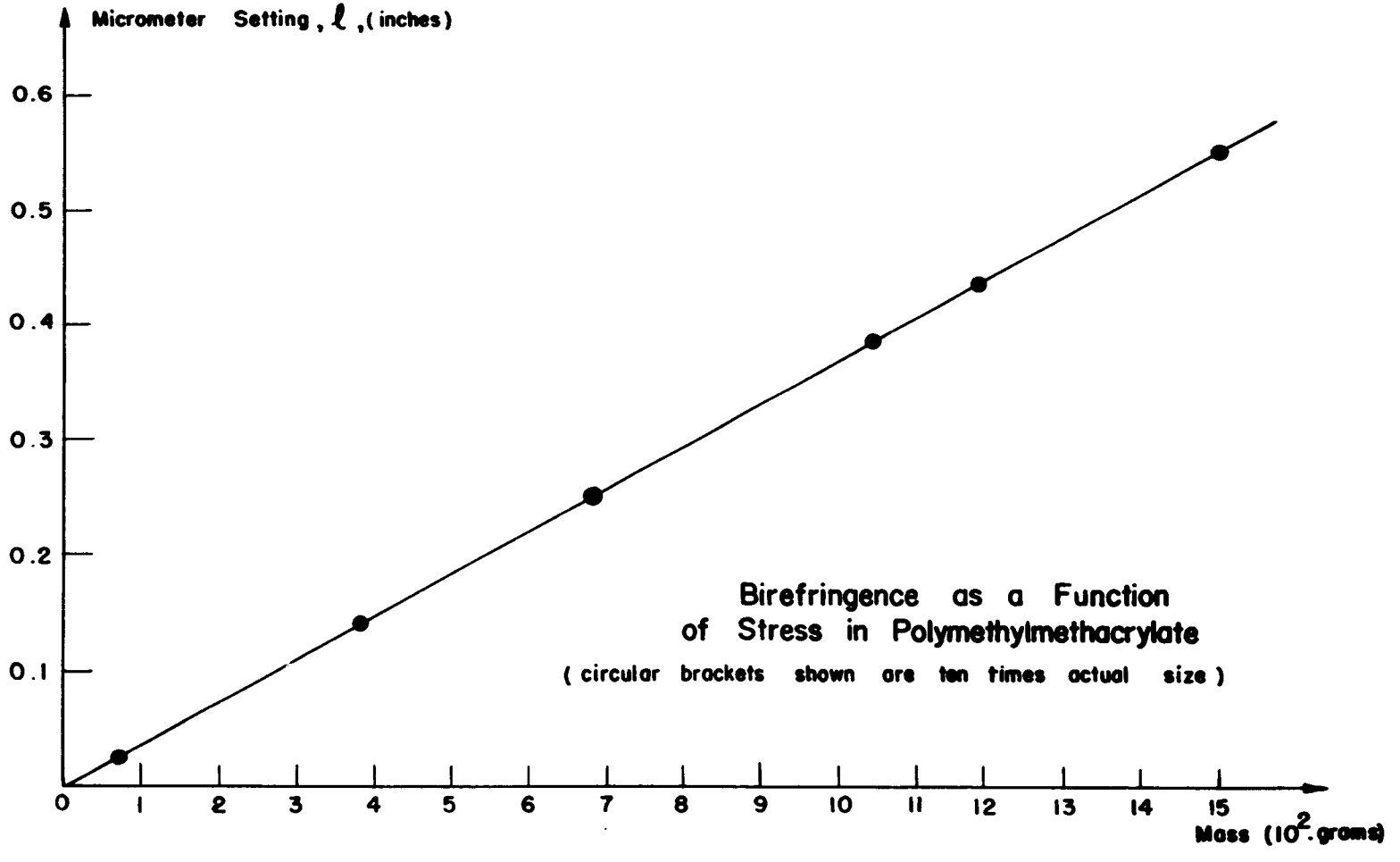

Micrometer Setting, ℓ, (inches)
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Mass (10^2 grams)
Birefringence as a Function
of Stress in Polymethylmethacrylate
(circular brackets shown are ten times actual size)

FIG. 3

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STUDY OF THE MOLECULAR STRESS RESPONSE OF SOLID POLYMERS
BY PHOTOELASTIC METHODS

R. D. Andrews, Jr.

Technical Report No. _____, Feb. 15, 1963, 12 pp., figures.
DA Proj. TB4-002; Contract No. DA-19-020-ORD-5213.
Unclassified title, report and cards; no distribution limitations.

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